Lawrence Berkeley Laboratory
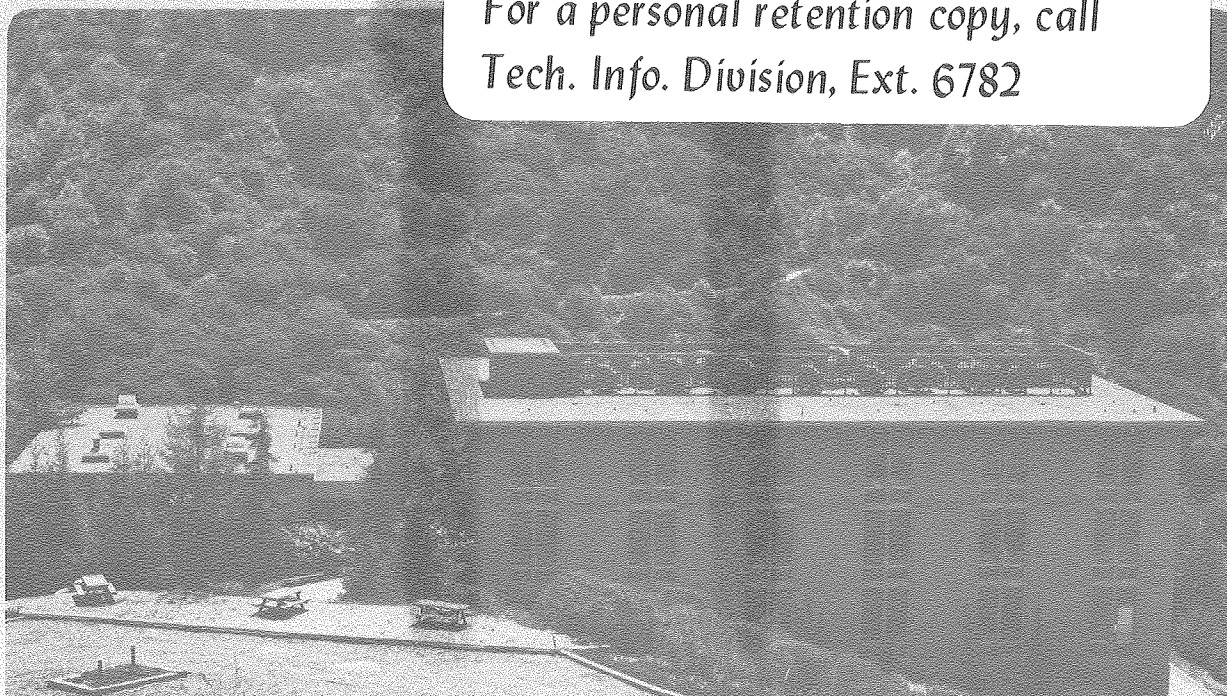## UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

INFLUENCE OF IMPURITIES ON HIGH TEMPERATURE REACTIONS OF KAOLINITE

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TEMPERATURE REACTIONS OF KAOLINITE

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ABSTRACT

On heating kaolinite in DTA the second exothermic peak ($\sim$1275°C)
is due to growth of mullite crystals accelerated by formation of a liquid
phase. The third exothermic peak ($\sim$1460°C) is due to crystallization of
cristobalite. Addition or presence of impurity oxides causes the second
peak to shift in temperature, and accelerates the formation of cristobalite
so that the third peak could appear as low as the second exothermic peak
temperature.

1. INTRODUCTION

The solid state reaction sequence on heating kaolinite has been widely studied[1-4] using differential thermal analysis (DTA). Most of the work has been centered on the nature of the first exothermic reaction (peak temperature ~980°C). However, investigations of the second exothermic reaction which occurs between 1200 and 1300°C and a third exothermic reaction at ~1400°C have not been as extensive. Previous observations have related these reactions to the presence of impurities and the state of order of the kaolinite.[5,6]

According to Glass,[5] thermograms from ordered kaolinite only showed the first and second exothermic peaks while an additional third exothermic peak at a higher temperature was observed for disordered kaolinites. The latter peak was attributed to the formation of cristobalite. Prabhakaram[6] attributed the position of the second exothermic peak to the degree of crystallinity of the kaolinite; the more ordered the mineral, the higher the peak temperature. Wahl and Grim[7] reported similar results. Smykatz-Kloss[8] attempted to determine the degree of order of kaolinite by DTA only using data obtained at temperatures below 1000°C.

Bulens and Delmon[9] claimed that additions of MgO to ordered and disordered kaolinites caused mullite formation via a spinel or γ-Al_2O_3 phase and that CaO caused mullite formation directly from metakaolinite. They said that the second exothermic peak (~1250°C) was absent in the samples to which CaO had been added. Wahl and Grim[7] added a number of impurities to well and poorly crystallized kaolinite and found a variable effect on the temperature of formation of mullite and cristobalite.

The purpose of the present work is to show that the size and temperature of the second and third exothermic peaks is related to the presence of impurity phases in the kaolinite (both type and amount) and thus only indirectly to the state of order of the mineral.

2. EXPERIMENTAL

An ordered (K Ga-1)* and disordered (K Ga-2)* kaolinite were used. For chemical analyses, see Table 1.*

CaO and K_2O were added to both kaolinites as nitrates. Mixing was done in a vibratory mill using alumina balls in isopropyl alcohol for 2 hours, followed by drying at 110°C for 24 hours. Bulens and Delmon[9] used an atomic proportion (M/Al+Si) of 0.063 Ca which is actually 4 wt.% CaO. This same amount of CaO was added to both kaolinites. Separate batches containing 1.5 wt.% K_2O were also prepared.

Differential thermal analyses (DTA) from room temperature to 1500°C at a heating rate of 10°C/min were performed on the samples with and without additives. X-ray diffraction analyses were performed on the ground samples heated to just after each of the exothermic peaks. These samples were also polished, etched with a 40% HF solution and studied by SEM and EDAX.

3. RESULTS AND DISCUSSION

Thermograms of various samples are shown in Fig. 1. X-ray diffraction patterns of heated ordered and disordered kaolinite (Fig. 2) indicate no crystallinity after the first exothermic peak at ∿1100°C (A caused by anatase present as impurity), mullite after the second exothermic peak at ∿1310°C, and

*Source Clays, Clay Minerals Society

both mullite and cristobalite after the third exothermic peak at $\sim$1465°C. With the addition of K_2O or CaO, cristobalite also appears with mullite after the second exothermic peak (Fig. 3).

The thermograms indicate that the first exothermic peak is narrow and remains essentially at $\sim$980°C in all cases. However, the assembled DTA data in Table 2 shows that the position of the second exothermic peak depends on the impurities present. The presence of CaO in the ordered kaolinite shifts the peak higher in temperature from 1275 to 1300°C while K_2O shifts it lower, from 1275 to 1250°C. The same trend occurs in disordered kaolinite, although to a lesser extent. The third exothermic peak is even more sensitive to impurities.

A significant observation is the appearance of a liquid phase after the second exothermic peak as indicated by examination of the photomicrographs obtained by SEM after etching shown in Figs. 4 and 5 of specimens K Ga-2 + 4% CaO and K Ga-1 + 4% CaO. A further indication of the appearance of a liquid phase at this point is the occurrence of shrinkage with an increase in strength of the specimens. The microstructures consist of large grains which were the original kaolinite particles (labeled A) and small crystals (labeled B) dispersed in a liquid phase. The indicated EDAX analyses show that the Al:Si ratio in the former is approximately 1:1 indicating that they most probably consist of mullite crystallites with the excess silica from the metakaolinite still present. The Al:Si ratio is closer to that for mullite in the dispersed smaller crystals that grew in the liquid phase which always had most of the impurities.

The impurities in the starting specimen can be considered to be of two types: crystallographic such as those associated with the grains

of disordered kaolinite, and separate phases such as the additives in this study. A number of reactions are going on with the dynamic increase of temperature of the DTA test. The kaolinite grains appear to be undergoing progressive reaction steps essentially independently. It has been proposed[10] that the first exothermic peak is the result of a nucleation process forming a population of mullite nuclei within the kaolinite grains irrespective of impurities which accounts for the constancy of the peak temperature. The second exothermic peak is the result of rapid growth of mullite crystals by a solution-precipitation mechanism generated by the appearance of a liquid phase. The basic source of this liquid in pure kaolinite is probably a metastable liquid involving amorphous silica and disordered mullite. A metastable eutectic at about 1200 to 1275°C has been previously reported.[11] The third exothermic peak is the result of a crystallization of cristobalite from the amorphous silica in the absence of, or presence of small amounts of, impurities.

The additives of K_2O and CaO (after decomposition of the respective nitrates) first undergo solid state reactions at contacts with the metakaolin grains since these mixtures are not in chemical equilibrium. These reactions continue with increasing temperature simultaneously with the reactions going on within the kaolinite grains. The impurity reaction products react with the liquid phase forming within the grains, causing the liquid composition and its properties to be modified and thus affecting the position of the second exothermic peak by accelerating the crystallization of cristobalite. The appearance of anatase at 1100°C and absence at 1300°C (Fig. 2) indicates that it apparently also is associated with the formation of this liquid. The approach to the phase compositions indicated by the stable phase equilibrium diagrams depends on the kinetics of the mentioned reactions which are

accelerated by an increase of the liquid phase. A significant approach to the equilibrium compositions under the DTA experimental conditions apparently occurs at about the temperature of the second exothermic peak but becomes more pronounced at the higher temperature of the third exothermic peak.

Since the additives affect the composition and properties of the liquid forming within the grains, the addition of K_2O to ordered kaolinite will shift the second exothermic peak towards the eutectic temperature of $\sim 1000°C$ as indicated for the overall composition in the equilibrium diagram for the ternary system $SiO_2-Al_2O_3-K_2O$ (Fig. 6).[12] When CaO is added, the second peak is shifted towards a higher temperature since the eutectic temperature is $\sim 1340°C$ in the system $SiO_2-Al_2O_3-CaO$. In the case of disordered kaolinite with more crystallographic impurities, the addition of K_2O or CaO exerts less influence on the second peak. In addition, the presence of a sufficient amount of impurities accelerates the crystallization of cristobalite causing the appearance of cristobalite with the mullite after the second peak. These interpretations are in agreement with the XRD analyses shown in Figs. 2 and 3: sample K Ga-1 shows sensitivity to the nature of the additive whereas K Ga-2 shows essentially no difference with additions of K_2O or CaO, the amount of mullite and cristobalite being substantially the same.

In order to understand more fully the nature of the phase compositions after the second and third exothermic peaks, we can assume for simplicity that all of the impurities in a kaolinite specimen are present as K_2O so that we can use the $SiO_2-Al_2O_3-K_2O$ phase equilibrium diagram (Fig. 6) as a guide. If equilibrium for the overall compositions were continually maintained, the resulting percentage phase compositions for

pure metakaolinite with 0.0, 0.5, 1.5, 4.1 and 5.0 wt.% of K_2O at 1100, 1200 and 1400°C would be as shown in Table 3. It can be seen that at a given temperature with increasing amounts of K_2O the amount of cristobalite decreases and the amount of liquid increases. In the real case, however, initially the dehydroxylated kaolinite undergoes decomposition reactions independently while the K_2O first reacts at interfaces to form compounds which subsequently react with the high silica phase in the grains to form liquids with higher K_2O content which are approaching equilibrium compositions. This sequence of reactions supports the experimental presence of more cristobalite in K Ga-2 than K Ga-1 after the second exothermic reaction and less after the third as shown schematically in the lower part of Fig. 6. The phase composition data also suggests that with a sufficient amount of impurities cristobalite will not appear during heating.

4. <u>SUMMARY</u>

It is evident that in starting out with an assembly of nonequilibrium phases within a given system, in this case the $SiO_2-Al_2O_3-K_2O$ system, the kinetics of side reactions play a critical role. Kaolinite, which becomes metakaolinite after dehydroxylation corresponding to the main endothermic peak in DTA, undergoes several successive reactions (represented by three exothermic peaks in a DTA run) in attaining the equilibrium phases of mullite and cristobalite. It has been postulated[10] that the first exothermic peak represents the formation of mullite nuclei. This study indicates that the second exothermic peak is the result of the rapid growth of mullite by a solution-precipitation process promoted by the formation of an amorphous or liquid-like silica-rich phase, and that

the third exothermic peak is the result of the crystallization and growth of cristobalite.

When additions of K_2O are made, solid state reactions occur at the metakaolinite grain contacts independently to form compounds which react with the precursor amorphous phase in the grain to form the modified liquid associated with the second exothermic peak. This reaction introduces some K_2O into the amorphous SiO_2-rich phase which causes an acceleration of the mullite growth with a shift of the second exothermic reaction peak to a lower temperature. A sufficient amount of K_2O addition also causes an acceleration of the crystallization and growth of cristobalite which would in turn cause the third exothermic peak eventually to merge with the second peak. Additions of CaO have a similar effect except that the peak temperature of the second exothermic reaction in the DTA is shifted to a higher temperature.

As the reactions proceed toward thermodynamic equilibrium, the amorphous phase in the original metakaolin grains becomes enriched in the additive oxide. Correspondingly, the cristobalite that had formed within the original kaolinite grains is taken into solution; an increase of additive accelerates the cristobalite solution as seen in Table 3. If the amount of additive is sufficient and the time is long enough and/or the temperature is high enough, all of the cristobalite will dissolve and the final equilibrium composition at temperature will consist of mullite and liquid. On cooling, the liquid phase in this composition range normally solidifies metastably as a glass with the possible precipitation of some secondary mullite.

ACKNOWLEDGMENT

Table 1. Chemical Analyses

Constituent	Ordered Kaolinite K Ga-1, wt%	Disordered Kaolinite K Ga-2, wt%
SiO_2	44.2	43.9
Al_2O_3	39.7	38.5
Fe_2O_3	0.13	0.98
FeO	0.08	0.15
TiO_2	1.39	2.08
CaO	N.D.	N.D.
MgO	0.03	0.03
Na_2O	0.013	<0.005
K_2O	0.050	0.065
MnO	0.002	N.D.
P_2O_5	0.034	0.045
S	N.D.	0.02
L.O.I.(550°C)	12.6	12.6
L.O.I.(550°C - 1050°C)	1.18	1.17
TOTAL	99.40	99.55

N.D. = not detected

Table 2. Position of Peaks

Material	2nd Exothermic, °C	3rd Exothermic, °C
Ordered Kaolinite		
K Ga-1	1275	1460
K Ga-1 + 4% CaO	1300	1460
K Ga-1 + 1.5% K_2O	1250	1425
Disordered Kaolinite		
K Ga-2	1250	1400
K Ga-2 + 4% CaO	1260	1435
K Ga-2 + 1.5% K_2O	1230	1360

Table 3. Equilibrium Phase Compositions on Heating Kaolinite with K$_2$O Additions at Several Temperatures

		0.0	0.5	1.5	4.1	5.0
1000°C	L	0	5.0	19.2	45.0	45.3
	M	64.0	64.0	60.1	55.0	52.1
	Cr*	36.0	31.0	20.9	0	-
	Fel	-	-	-	-	2.6
1200°C	L	0	6.0	23.6	46.8	48.4
	M	64.0	63.1	59.7	53.2	51.6
	Cr*	36.0	30.9	16.7	0	-
	Fel					0
1400°C	L	0	11.8	42.2	48.6	50.8
	M	64.0	62.0	57.8	51.4	49.2
	Cr*	36.0	26.2	0	0	-
	Fel					0

L = liquid, M = mullite, Fel = potash feldspar, Cr* = cristobalite (the stable polymorphic phase of silica in this temperature range is tridymite, but cristobalite is the only crystalline phase that appears).

With 0.5 wt% of K$_2$O cristobalite melts at ∿1560°C; 1.5 wt%, at ∿1400°C; 4.1 wt%, ∿1000°C; 5.0 wt%, no cristobalite above eutectic temperature of 985°C and feldspar melts at ∿1100°C.

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FIGURE CAPTIONS

Fig. 1.   DTA's of K Ga-1 and K Ga-2 and with additives of 4% CaO, 1.5% K_2O.

Fig. 2.   XRD's of K Ga-1 and K Ga-2 after 1100, 1310 and 1465°C.

Fig. 3.   XRD's of K Ga-1 and K Ga-2 and with additives of 4% CaO, 1.5%
          K_2O after 1310°C.

Fig. 4.   SEM photomicrograph of etched specimen of K Ga-2 + 4% CaO after
          1310°C, and EDAX analyses of grains A and B.

Fig. 5.   SEM photomicrograph of etched specimen of K Ga-1 + 4% CaO after
          1310°C, and EDAX analyses of grains A and B.

Fig. 6.   Part of equilibrium phase diagram for SiO_2-Al_2O_3-K_2O system
          showing cooling paths for dehydroxylated K Ga-1 and K Ga-2,
          equivalent to metakaolinites with additions of K_2O. Lower
          sketch: Schematic of cristobalite content with temperature for
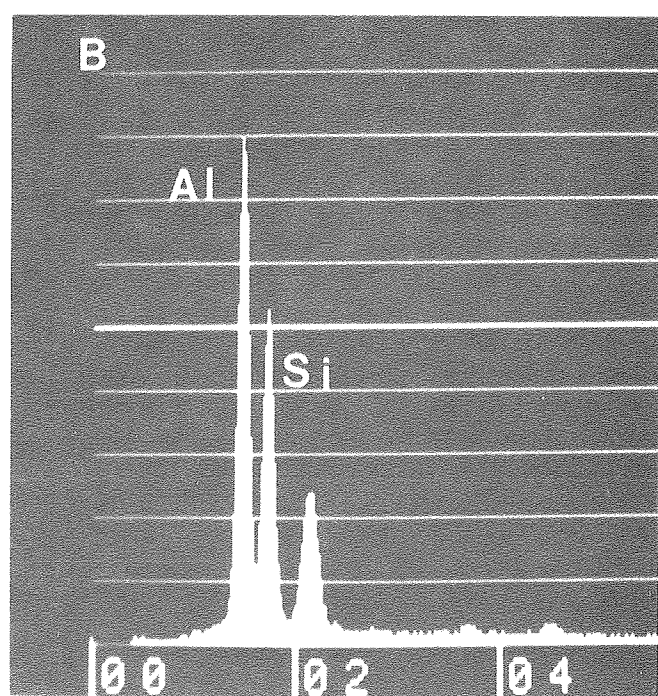   both specimens.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

10 μm

XBB800-11984

Fig. 5

SiO$_2$
1723°

Cristobalite

~1590°
1470°
1465°

Tridymite

985°

Quartz

'Cristobalite' + Mullite + Liquid boundary

Potash Feldspar

1140°

KGa-2
KGa-1
Metakaolinite (Al$_2$O$_3$·2SiO$_2$)

Mullite

3Al$_2$O$_3$·2SiO$_2$
~1840°

K$_2$O

Al$_2$O$_3$

% Cristobalite

KGa-2

KGa-1

1465

Temperature, °C

XBL8010-6018

Fig. 6